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Oxidative Dehydrogenation of Ethane over Sn-W-O_x Catalysts

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Abstract

The oxidative dehydrogenation of ethane to ethene was investigated over the catalyst composed of tin and tungsten oxides at 923 K under atmospheric pressure. A pure SnO_2 catalyst showed the high ethane conversion but low ethene selectivity (the major product was carbon dioxide). On the other hand, a pure WO_3 catalyst showed the high ethene selectivity while the ethane conversion was relatively low. The remarkable synergetic effect of tin and tungsten was observed when $Sn_2W_3O_8$ was used as catalyst precursor. According to the XRD measurement, $Sn_2W_3O_8$ was found to decompose into SnO_2 and WO_3 after the reaction, however, no significant difference was observed in the XPS analysis for tin and tungsten between the samples before and after the reaction. To clarify the synergism of tin and tungsten in $Sn_2W_3O_8$, the Auger parameter was employed for the surface oxygen atom of the catalyst. The clear relationship was found between the ethene yield and the ionicity of the oxygen atom.

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Keywords: auger parameter, dehydrogenation, ethane, tin oxide, tungsten oxide.

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1. Introduction

Ethene, which is one of the most important raw materials in the chemical industry, is mainly produced by steam cracking of ethane or naphtha at the higher temperatures than 1000 K. Under the reaction conditions of the high temperature and low oxygen concentration, the undesired side reactions, such as coke formation and C-C bond cleavage, take place [1]. The oxidative dehydrogenation of ethane (ODE) can offer a low cost and energy saving process for the ethene production because the reaction is exothermic and suppresses the coke formation.

Molybdenum [2] and vanadium [3] are known as the popular catalyst elements for the ODE and their reaction mechanism and kinetics are investigated in detail [3], [4]. However, the effective catalyst has not been developed due to the difficulty of the C-H bond activation in ethane at low temperatures.

In this study, the ODE over the catalysts composed of tin and tungsten oxides is presented and the catalytic activity is discussed with respect to the electronic state of the surface oxygen atom of the catalyst.

2. Experimental

All chemicals and solvents were of the highest grade where obtainable and were used without further purification.

2.1. Preparation of catalysts

Sn/WO_3: Tungsten oxide was impregnated with toluene solution of tin octanoate. The solvent was removed at 393 K and the sample was calcined in air at 973 K for 3 h.

W/SnO_2: Tin oxide was impregnated with an aqueous solution of ammonium tungstate and the sample was calcined in air at 973 K for 3 h.

$Sn_2W_3O_8$: The physically mixed tungsten oxide, tin oxide, and tungsten powders were heated in vacuo at 973 K for one week [5].

2.2. Activity test

The activity test was carried out with a flow-type fixed-bed reactor (quartz, 6 mm i.d.) under atmospheric pressure as shown in Figure 1. The length of the heating zone by an electric furnace is 300 mm. The catalyst was placed at the center of the reactor and each reactant gas was supplied through a mass flow controller (MFC).

The catalyst was pretreated with nitrogen gas stream under atmospheric pressure at 973 K for 0.5 h. After enough cooling, a reactant gas mixture (nitrogen/ethane/oxygen=7/2/1) was introduced at SV=30,000 mL g-cat^{-1} h^{-1} and the temperature was set. The effluent gas was analyzed by an on-line gas chromatograph (Porapak Q for CO_2, ethane, and ethene; MS-5A for CO and methane) equipped with a thermal conductivity detector.

2.3. Characterization of catalysts

The X-ray diffraction (XRD) measurement was carried out by using RINT2000 diffractometer (Rigaku Corp., Japan) with Cu Kα radiation. The surface analyses by X-ray photoelectron spectroscopy (XPS) were performed with ESCA-3200 (Shimadzu Corp., Japan) using magnesium radiation (8 kV, 30 mA). After enough cooling, the sample was taken out from the reactor and was set to the sample holder of the XPS instrument. The spectra were recorded after argon-ion etching for 0.5 min (2 kV, 25 mA). The values of binding energy were corrected with that of C(1s) (284.6 eV) for carbon contaminant [6].

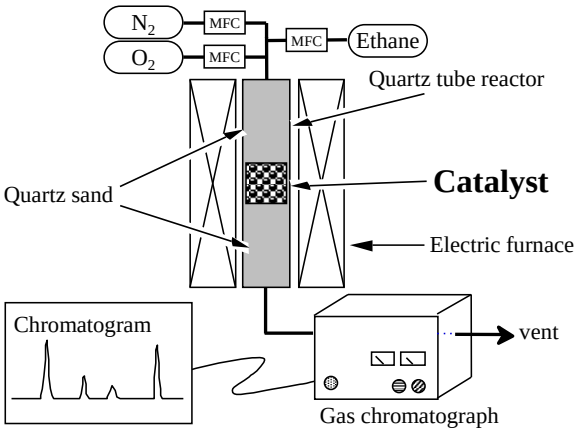

Fig. 1. Flow-type fixed-bed reactor.

3. Results and discussion

3.1. Catalytic activity of Sn-W-O_x catalysts

The ODE was carried out using the empty reactor at 973 K, where the gas phase (or non-catalytic) reaction may take place. As shown in Table 1, the ODE without catalyst gave 64% ethane conversion and 67% ethene selectivity (Entry 1). Interestingly, almost the same catalytic activities (conversion and selectivity) were obtained over SnO_2 or WO_3 catalyst (Entries 2 and 3). When the reactor was fully filled with quartz sand (50-70 mesh), the ethane conversion was only 1.7% (Entry 4). These results indicate that the gas phase reaction should be suppressed to evaluate the 'true' catalyst property, then the open space of the reactor was filled with quartz sand to avoid the non-catalytic reaction for the further experiments.

Since the catalytic activity is strongly affected by the nature of the support, the interaction between the catalyst and the support has been investigated in the ODE so far and the well-dispersed catalyst on the support is believed to have the high catalytic activity [3]. In the present study, three types of the catalyst composed of tin and tungsten were prepared: the tin catalyst supported on WO_3 (Sn/W=0.00050 in atomic ratio, Sn/WO_3), the tungsten catalyst supported on SnO_2 (W/Sn=0.0066, W/SnO_2), and the tin and tungsten composite oxide catalyst $Sn_2W_3O_8$.

Table 1. Product distribution of the ODE at 973 K.

Entry	Catalyst	Conv.(%)	Selectivity(%) [a,b]			
			$C_{2=}$	C_1	CO	CO_2
1	none	64	67	8.9	23	0.8
2	SnO_2	62	66	7.9	25	1.6
3	WO_3	64	67	7.9	24	1.1
4	blank	1.7	98	2.3	0	0

Conditions: see the experimental section for the details.
[a] Calculated on the basis of carbon-mol. [b] $C_{2=}$ and C_1 represent ethene and methane, respectively.

Table 2. Catalytic activity of Sn-W-O_x catalysts for ODE.

Catalyst	Temp. (K)	Conv. (%)	Selectivity(%)				$C_{2=}$ yield (%)
			$C_{2=}$	C_1	CO	CO_2	
Sn/WO_3	923	14	84	2.8	14	0	12
W/SnO_2	723	17	38	0	17	45	6.5
$Sn_2W_3O_8$	973	18	83	3.5	8.8	5.1	15
SnO_2	723	19	30	0.8	4.7	65	5.6
WO_3	923	13	88	2.8	9.6	0	11

Conditions: see the experimental section.

Although the tin in the Sn/WO_3 and the tungsten in the W/SnO_2 are present as the oxide form on the support, they are denoted as Sn/WO_3 and W/SnO_2, respectively, for convenience. The composite oxide $Sn_2W_3O_8$ can be considered as one example of the highly dispersed catalyst with respect to tin and tungsten in atomic level.

The catalytic activity of the tin and tungsten containing catalysts for the ODE is summarized in Table 2. To discuss the product distribution, the ethane conversion was roughly adjusted to the comparable values (14-18%) by changing the reaction temperature. Unexpectedly, the Sn/WO_3 and W/SnO_2 catalysts showed almost the same catalytic activities as those of the support materials, meaning that the loaded elements may not have been enough dispersed.

It is noteworthy that $Sn_2W_3O_8$ showed 15% ethene yield and 83% selectivity even at 973 K. The product distribution was significantly different from that obtained by the gas phase reaction (see Table 1; Entry 1). This means that $Sn_2W_3O_8$ acts as a catalyst under the reaction conditions. In addition, the product distribution was different from those obtained by the reaction over SnO_2 or WO_3. It can be concluded that the synergism of tin and tungsten resulted in the high ethene yield.

3.2. Characterization of $Sn_2W_3O_8$

Figure 2 shows the XRD patterns of the $Sn_2W_3O_8$ sample before and after reaction. The clear pattern of $Sn_2W_3O_8$ was found before reaction although some ambiguous peaks assignable to the starting materials were recorded (Figure 2(a)). On the other hand, the mixed phases of WO_3 and SnO_2 were observed after reaction, while the $Sn_2W_3O_8$ phase almost disappeared (Figure 2(b)).

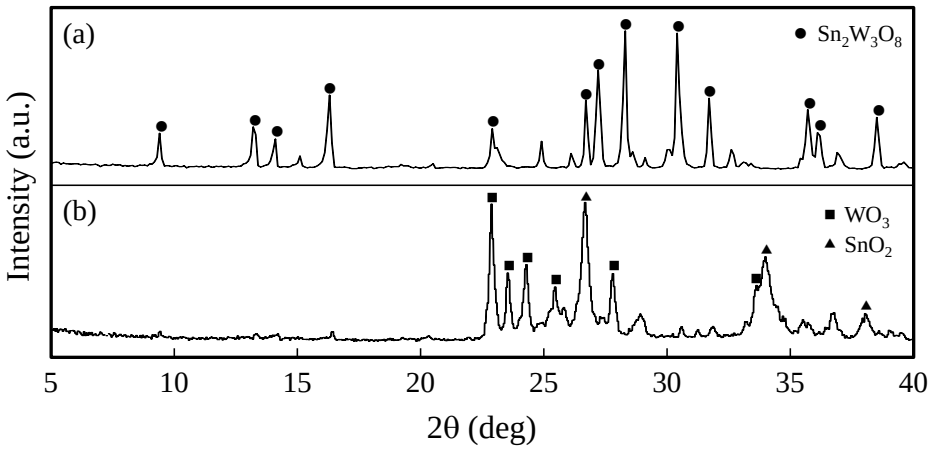

Fig. 2. XRD patterns of $Sn_2W_3O_8$: (a) before and (b) after reaction.

According to the XPS analysis, no significant difference was observed for tin and tungsten between the samples of the before and after reaction.

3.3. Property of the lattice oxygen on the catalyst surface

To clarify the synergism of tin and tungsten in $Sn_2W_3O_8$ sample after the reaction, Auger parameter was employed for the characterization of the lattice oxygen atom on the catalyst surface. The Auger parameter (α) is defined as shown in equation (1):

$$\alpha = BE(O\ 1s) + KE(O\ KLL) \quad (1)$$

where BE is the binding energy and KE is the kinetic energy of the emitted electrons [7], [8]. The smaller α value corresponds to the higher ionicity.

Figure 3 shows the plots of the ethene yield obtained over tin and/or tungsten containing catalysts as a function of the Auger parameter (α). It is clearly seen that the lattice oxygen with the high ionicity leads to the high ethene yield when the ethane conversion is almost the same. On the other hand, the C-C bond cleavage occurs when the ionicity is not so high, resulting in the high selectivities to methane, carbon monoxide, and carbon dioxide.

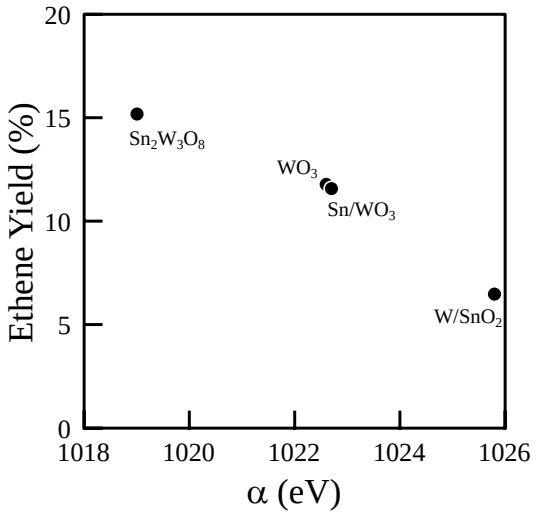

Fig. 3. Plots of ethene yield vs Auger parameter for O(1s).

4. Conclusion

The composite oxide catalyst $Sn_2W_3O_8$ showed the high selectivity to ethene in ODE at 973 K. The product distribution is significantly different from those obtained by SnO_2, WO_3, and the gas phase (non-catalytic) reaction. According to the XRD measurement, $Sn_2W_3O_8$ was found to decompose into SnO_2 and WO_3 after the reaction. The synergetic effect of tin and tungsten was found only when $Sn_2W_3O_8$ was used as a catalyst precursor. No significant synergism of tin and tungsten was observed by XPS analysis, then the Auger parameter of the surface oxygen atom was employed for the catalyst characterization. A high ionicity of the surface oxygen on the catalyst is one of the important factors to produce ethene in the ODE. These findings can contribute to the development of more active catalysts for the ODE at low temperatures.

Acknowledgements

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